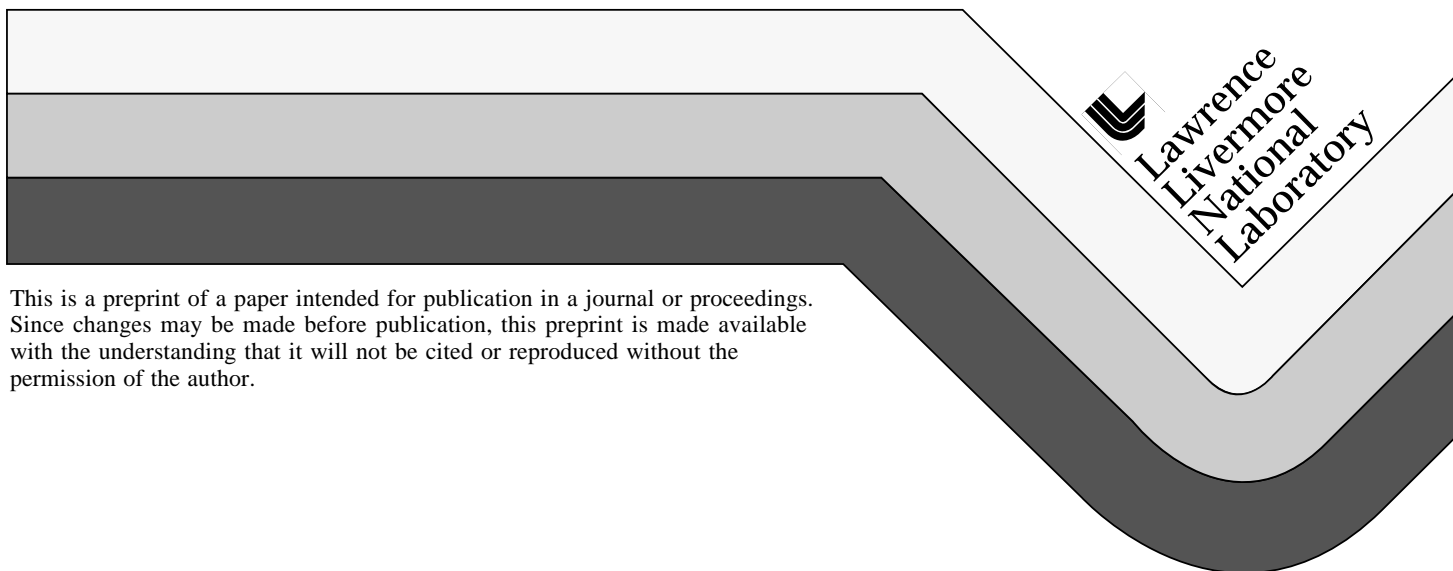# Ion Sorption onto Hydrous Ferric Oxides: Effect on Major Element Fluid Chemistry at Äspö, Sweden

Carol J. Bruton
Brian E. Viani

This paper was prepared for submittal to the
Second Äspö International Geochemistry Workshop
Äspö, Sweden
June 6-7, 1995

June 1996

Lawrence Livermore National Laboratory

DISCLAIMER

ION SORPTION ONTO HYDROUS FERRIC OXIDES: EFFECT ON MAJOR ELEMENT FLUID CHEMISTRY AT ÄSPÖ, SWEDEN

Carol J. Bruton and Brian E. Viani
Lawrence Livermore National Laboratory
Livermore, California 94550 USA

ABSTRACT

The observed variability of fluid chemistry at the Äspö Hard Rock Laboratory is not fully described by conservative fluid mixing models. Ion exchange may account for some of the observed discrepancies. It is also possible that variably charged solids such as oxyhydroxides of Fe can serve as sources and sinks of anions and cations through surface complexation. Surface complexation reactions on hydrous ferric oxides involve sorption of both cations and anions.

Geochemical modeling of the surface chemistry of hydrous ferric oxides (HFOs) in equilibrium with shallow HBH02 and deep KA0483A waters shows that HFOs can serve as significant, pH-sensitive sources and sinks for cations and anions. Carbonate sorption is favored especially at below-neutral pH. A greater mass of carbonate is sorbed onto HFO surfaces than is contained in the fluid when 10 g goethite, used as a proxy for HFOs, is in contact with 1 kg H_2O. The masses of sorbent required to significantly impact fluid chemistry through sorption/desorption reactions seem to be reasonable when compared to the occurrences of HFOs at Äspö. Thus, it is possible that small changes in fluid chemistry can cause significant releases of cations or anions from HFOs into the fluid phase or, alternately, result in uptake of aqueous species onto HFO surfaces.

Simulations of the mixing of shallow HBH02 and native KA0483A waters in the presence of a fixed mass of goethite show that surface complexation does not cause the concentrations of Ca, Sr, and SO_4 to deviate from those that are predicted using conservative mixing models. Results for HCO_3 are more difficult to interpret and cannot be addressed adequately at this time.

In future work, the effect of surface complexation on the partitioning of trace elements such as uranium between HFOs and ground water will be addressed.

1   INTRODUCTION

Laaksoharju (1994) noted that conservative fluid mixing models do not adequately describe fluid chemistries resulting from mixing of waters at the Äspö Hard Rock Laboratory. In particular, calcium, sodium, carbonate and sulfate were not conserved during fluid mixing. Viani and Bruton (1994) showed that fixed charge ion exchangers such as smectite can serve as sources and sinks of Na^+, Ca^{++} and Mg^{++}, and may have

contributed to non-conservative fluid mixing during the Large Scale Redox Experiment. It is also possible that variably charged solids such as oxyhydroxides of Fe can serve as sources and sinks of anions and cations and thus impact fluid chemistry.

A variety of cations (e.g. H^+, Ca^{++}, Sr^{++}, Ba^{++}) and anions (HCO_3^-, SO_4^{--}, HPO_4^-) are known to sorb onto hydrous ferric oxides (HFOs) at 25^oC (Dzombak and Morel, 1990). Hematite and Fe-oxyhydroxide are commonly found as fracture fillings at Äspö (e.g., Tullborg, 1995; Landstrom and Tullborg 1994). Banwart et al. (1994) estimated that the abundance of hematite in altered granite is 1-2%, and that the abundance of Fe(III)-oxyhydroxides in the fracture coatings is 4%. Microfractures close to the fracture surface contain what appears to be iron oxyhydroxide. The ultimate goals of this work are to determine whether ion sorption onto HFOs during fluid mixing at Äspö can affect fluid chemistry, and to help test hypotheses regarding the mobility and partitioning of trace elements put forth by Landström and Tullborg (1995).

In this paper, we address the extent to which ion sorption and desorption can impact fluid chemistry at Äspö, and estimate the magnitude of the ion reservoirs (and sinks) represented by HFOs. An example will be shown of the effect on fluid chemistry of mixing of shallow and deep waters in the presence of HFOs at Äspö.

1.1   APPROACH

The approach in this paper is similar to that taken by Viani and Bruton (1994) to test the hypothesis that ion exchange affects the composition of groundwaters sampled from boreholes in the HRL tunnel. Geochemical modeling computer codes containing surface complexation models capable of simulating sorption onto HFOs were used to:

1) Calculate the potential for HFOs to serve as reservoirs and sinks of ions. The dependencies of ion sorption on pH in shallow and deep waters from the Redox Zone at Äspö were calculated to evaluate the potential for changes in major element chemistry during fluid mixing owing to the sorptive behavior of HFOs.

2) Simulate mixing between the shallow and deep waters that are believed to contribute to the observed changes in fluid chemistry with time in the Large Scale Redox Experiment. Contributions from Baltic and modified Baltic sea waters, proposed by Skarman and Laaksoharju (pers. comm.), are not considered in this set of calculations.

1.1.1   Surface complexation versus ion exchange

Surface complexation refers to chemical reactions between reactive functional groups exposed on a solid surface and aqueous species in an adjacent fluid. Surface complexation reactions lead to the sorption and desorption of anions and cations. The reactive functional groups at the solid surface (often referred to as "sites") derive from unsatisfied bonds created by the discontinuity of a three-dimensional structure.

The reactive sites on the surfaces of oxide minerals may be negative, neutral or positive depending on the extent of their protonation. Hence, the net charge on the surface may be positive or negative, depending on the pH of the solution. Oxide surfaces can therefore sorb anions as well as cations. In contrast, ion exchange minerals possess fixed amounts of charge imbalance, often imposed by the substitution of Al for Si in the mineral structure. The negative charge imbalance in cation exchangers restricts their exchange to cations. Hydrous ferric oxides with large specific surface areas on the order of 600 m^2/g have a sorptive capacity roughly equivalent to that of smectite when related on a per mole of sorbent basis.

Both surface complexation and ion exchange reactions vary as a function of aqueous complexation in the fluid phase, ionic strength, and the solid:fluid ratio. Surface complexation varies as a function of electrostatic effects as well, whereas ion exchange is sensitive to steric constraints imposed by the structure of the ion exchanger. Because the charge of reactive sites in oxides is controlled by pH, surface complexation reactions are much more sensitive to pH than ion exchange; the extent of ion sorption can change drastically within a few pH units.

1.2   <u>SURFACE COMPLEXATION MODELS</u>

The surface complexation reactions comprising the sorption model are provided for in the React geochemical modeling code. React is a part of The Geochemist's Workbench^{TM} set of software tools for calculating fluid-mineral-gas equilibria. React combines the calculational abilities of EQ3 and EQ6. EQ3/6, used by Viani and Bruton (1994) to describe ion exchange, could not be used as it does not provide for surface complexation reactions.

React can simultaneously provide for aqueous speciation in the fluid phase, mineral dissolution and precipitation, and surface complexation onto a sorbent, such as HFO. However, mineral dissolution and precipitation reactions were not considered in the calculations described in this paper.

React employs the generalized two-layer surface complexation model of Dzombak and Morel (1990). The generalized two-layer model is an extension of the diffuse double layer model, with provision for two types of sorption sites (weak and strong) and surface precipitation (see Dzombak and Morel, 1990 for an extensive discussion of the models).

1.3   <u>SIMULATION INPUT</u>

1.3.1   <u>Thermodynamic and sorption data</u>

Thermodynamic data for minerals, aqueous species and gases are contained in the React data base, which is sourced from an older version of the EQ3/6 data base called version R54. For the simulations described in this paper, however, the older data set should yield similar results to the current EQ3/6 data base GEMBOCH com.R22.

React contains a data base of surface complexation constants from Dzombak and Morel (1990) assuming a generalized two-layer surface complexation model. Although the most comprehensive compilation of constants to date, Dzombak and Morel's data set lacks complexation constants for carbonate species.

At low pH values, anions such as sulfate and carbonate tend to be sorbed by HFOs. Preliminary calculations with Dzombak and Morel's data set suggested that sulfate surface complexes dominate the total mass of sulfate in the fluid+sorbent system. However, the Dzombak and Morel (1990) data set does not provide for competition between sulfate and carbonate for sorption sites. Therefore, a literature search was made to identify experimental studies yielding carbonate complexation constants that could be added to the Dzombak and Morel (1990) data set.

Waite et al. (1994) determined carbonate complexation constants as part of a larger study to measure U(VI) sorption onto HFOs. They used a two-site diffuse double layer model. Van Geen, Robertson and Leckie (1994) focused on complexation of carbonate species at the goethite surface, and used a single-site diffuse double layer model to extract complexation constants from their sorption experiments.

The complexation constants from both papers were incorporated into two new versions of the React complexation constant data base from Dzombak and Morel (1990) (see Appendix A). Simulations were carried out with each of the three data bases (a) Dzombak and Morel (1990), (b) Dzombak and Morel plus carbonate complexation data from Waite et al. (1994), and (c) Dzombak and Morel plus carbonate complexation data from Van Geen, Robertson and Leckie (1994) for comparison.

Scoping calculations using all three data bases suggested that the data of Van Geen, Robertson and Leckie (1994) predicted significantly greater amounts of carbonate sorption than data from Waite et al. (1994). Van Geen, Robertson and Leckie's (1994) study also focused more closely on carbonate sorption than Waite et al. (1994). Thus, the two data bases from (a) Dzombak and Morel (1990) and (b) Dzombak and Morel plus carbonate complexation data from Van Geen, Robertson and Leckie were used to explore the impact of sorption on fluid chemistry in this contribution.

1.3.2   <u>Naming conventions for surface species</u>

In this paper, the naming conventions of Dzombak and Morel (1990) for surface complexes are used. "Weak" surface complexes are prefixed by ">(w)", whereas strong complexes are prefixed by ">(s)" (see Dzombak and Morel (1990) for a complete discussion of these species).

No distinction was made between strong and weak sites in Van Geen, Robertson and Leckie's (1994) one-site model. Nonetheless, the data for carbonate surface species had to be input to the Dzombak and Morel data base using the two-site designations. Accordingly, the complexation constants for strong and weak carbonate surface species

are equal, and the concentrations of strong and weak complexes of the same species should be added together to obtain the total molality of that surface species.

1.3.3 Solid sorbent

For the calculations in this paper, goethite was used as a proxy for a variety of iron oxyhydroxides such as ferrihydrite and hematite that can act as sorbents. Goethite was assumed to contain 0.205 moles of sorption sites (0.2 weak, 0.005 strong) per mole of Fe (Dzombak and Morel, 1990). Iron oxyhydroxides can vary significantly in terms of their surface area and corresponding total number of surface sites per mole of Fe. However, by relating our calculations to the number of surface sites available for reaction, we obtain a common frame of reference for all forms of HFOs. The mass of goethite per kilogram of H_2O was varied from 0.1 to 10 g/kg H_2O to illustrate the effects of variations in sorbent:fluid ratio. The relations between mass of goethite, number of surface sites and fluid mass are discussed later in the paper.

1.3.4   Fluid compositions

Fluid sample HBH02-910912 (Banwart et al., 1992) was considered to be representative of shallow waters. The deep, native water was represented by fluid sample KA0483A-910312 (Banwart et al., 1992). The scoping calculations described in this paper focus on major element chemistry; trace elements will be considered in future studies.

2   RESULTS

2.1   SORPTION ONTO HFOs IN SHALLOW WATERS

2.1.1 Calculations using surface complexation data base excluding carbonate surface species

The surface complexation reactions of goethite in HBH02 water are shown in Figures 1a and 1b as a function of pH using the carbonate surface species-free data base of Dzombak and Morel (1990). One gram of goethite, serving as a proxy for Fe-oxyhydroxides, was assumed to be in contact with 1 kg of H_2O with the composition of HBH02. Figure 1a illustrates the tendency of ions to sorb and desorb as pH varies. The identity and quantity of the surface species contributing to the sorbed fraction is shown in Figure 1b.

Sorbed fraction in Figure 1a refers to the fraction of a given element that resides on HFO surfaces relative to the total amount of that element in the fluid+sorbent system. It is calculated as the sum of the concentrations of sorbed species containing a given element, divided by the sum of the amount of the element in solution and the amount of the element sorbed. For example, a sorbed fraction of 0.5 implies that if there are 100 mg/kg SO_4 in solution, 100 mg/kg SO_4 are bound to the HFO surface as surface complexes.

The sorbed fraction is a useful measure of the effectiveness of a sorbent as a reservoir of ions. When the sorbed fraction exceeds 0.5, the mass of the sorbed element is greater than that in the fluid. A change in solution composition, such as pH, could release those ions and significantly increase the ion concentration in the fluid.

Figures 1a and b suggest that a significant quantity of SO_4 is associated with HFOs at pH values below neutral, even in the presence of only 1 gram of goethite. Surface complexation of SO_4 at alkaline pH values is negligible. In keeping with the general rule in surface complexation (Dzombak and Morel, 1990), low pH favors sorption of anions, whereas high pH favors cation sorption. Figure 1b shows the increase in the SO_4-bearing surface species as pH decreases, and of the Ca-bearing species as pH increases.
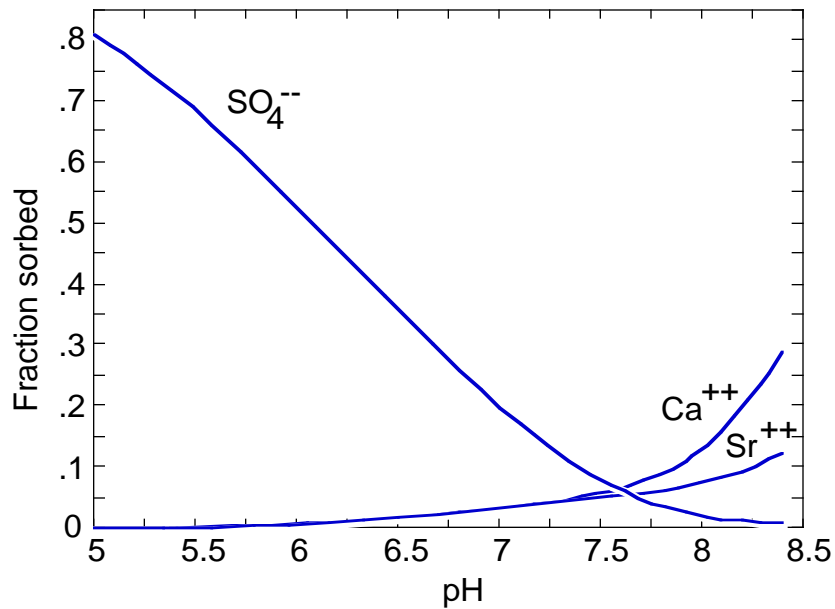
Figure 1a. Fraction of total quantity of SO_4, Ca and Sr sorbed onto 1 g goethite/kg H_2O in HBH02 water at 25°C using Dzombak and Morel (1990) surface complexation data base. Electrical balancing on HCO_3.
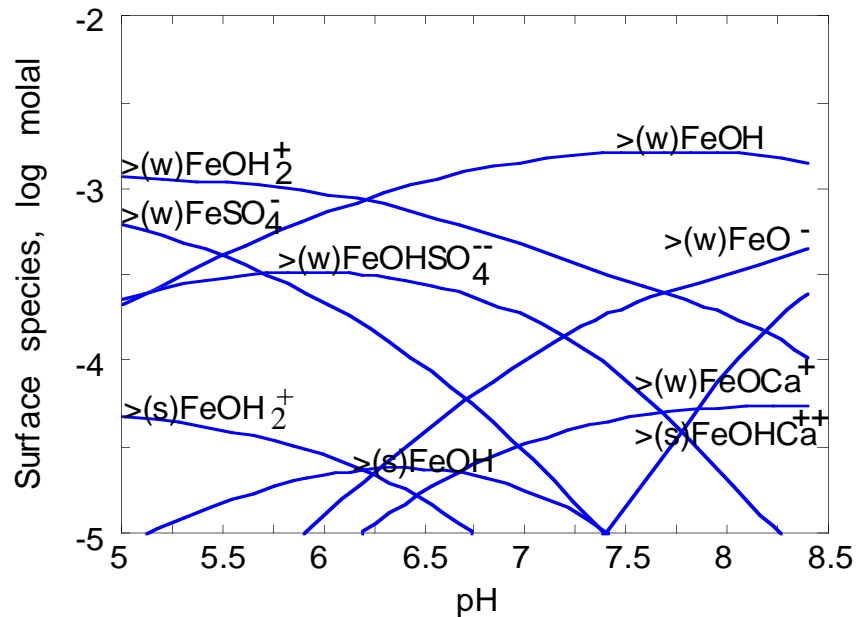

Figure 1b. Concentration of surface complexes on 1 g goethite/kg H_2O in HBH02 water at 25°C using Dzombak and Morel (1990) surface complexation data base. Electrical balancing on HCO_3. Concentration of surface complexes expressed as moles of complex per kg of H_2O, i.e. molality.

The impact of changing the sorbent:fluid ratio is addressed in Table 1, which shows the variation of sorbed fractions and concentrations of sorbed species as a function of the mass of goethite per kilogram of H_2O for the carbonate surface species-free system. The fluid composition is that of HBH02 with its pH set at 6.6, as measured. Larger goethite:solution ratios increase the concentrations of sorbed ions and the fraction sorbed. Given 1 gram of goethite per kilogram H_2O, as much SO_4 is sorbed on the solid as exists in solution. When the mass of goethite increases to 10, the vast majority of SO_4 in the fluid+HFO system resides on the goethite surface (216 vs 20 mg/kg).

Results for the shallow HBH02 water shown in Figures 1a and listed in Table 1 do not agree exactly because of differences in constraints used for the two sets of calculations. React, when calculating the reaction path that was represented by increasing the pH from 5 to 8.5, included the sorbed fraction in the starting system at pH= 5 as part of the total elemental mass in the system. As pH increases, anions such as SO_4 are released and cause the fluid composition to deviate from that of HBH02. Nonetheless, figures such as Figure 1a demonstrate the expected trends in sorptive behavior with pH. The effect in the deeper KA0483A waters is less pronounced because the calculated sorbed fraction at the starting pH of 5 is lower, and thus a smaller reservoir of ions is available to contribute to changes in solution composition.

2.1.2 Calculations using surface complexation data base including carbonate surface species

For comparison to Figures 1a and 1b, the same calculations as above were made incorporating data for the carbonate surface species from Van Geen, Robertson and Leckie (1994) into the Dzombak and Morel (1990) data base. These results are shown in Figures 2a and 2b and Table 2. It is apparent that carbonate species are sorbed at the expense of sulfate. Sulfate surface complexes drop to low concentrations because of competition from carbonate for surface sites. Carbonate surface complexes comprise a significant fraction of total carbonate in the fluid+sorbent system. For example, Table 2 shows that over 10 times as much carbonate (1121 mg/kg expressed as bicarbonate) is sorbed onto HFO surfaces as is contained in the fluid (114 mg/kg) given a sorbent:fluid ration of 10 g of goethite per kilogram of H_2O. Thus, the calculations suggest that HFOs at shallow depths may serve as important reservoirs or sources of carbonate if conditions, such as an increase in pH, favor desorption of carbonate.
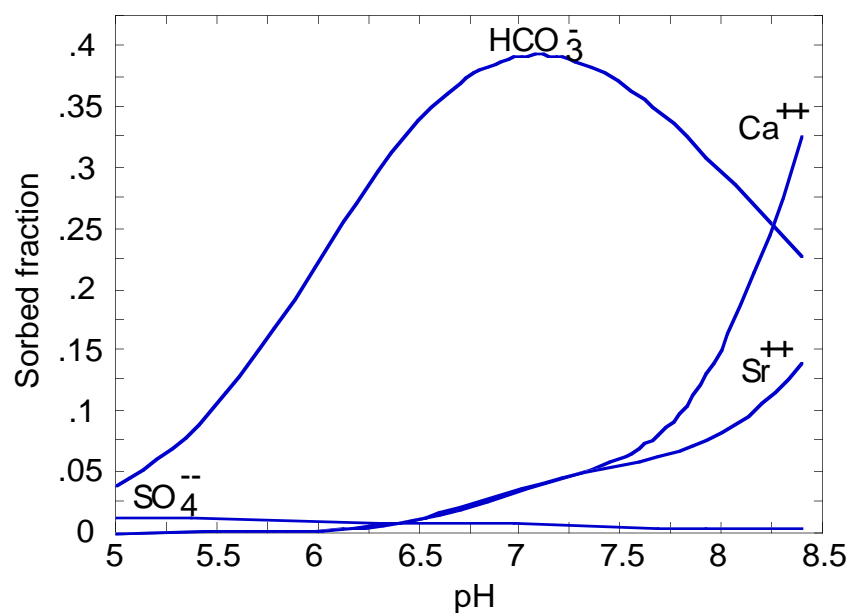
Figure 2a. Fraction of total quantity of HCO_3, SO_4, Ca and Sr sorbed onto 1 g goethite/kg H_2O in HBH02 water at 25°C using Dzombak and Morel (1990) surface complexation data with carbonate surface species from Van Geen, Robertson and Leckie (1994). Electrical balancing on HCO_3.
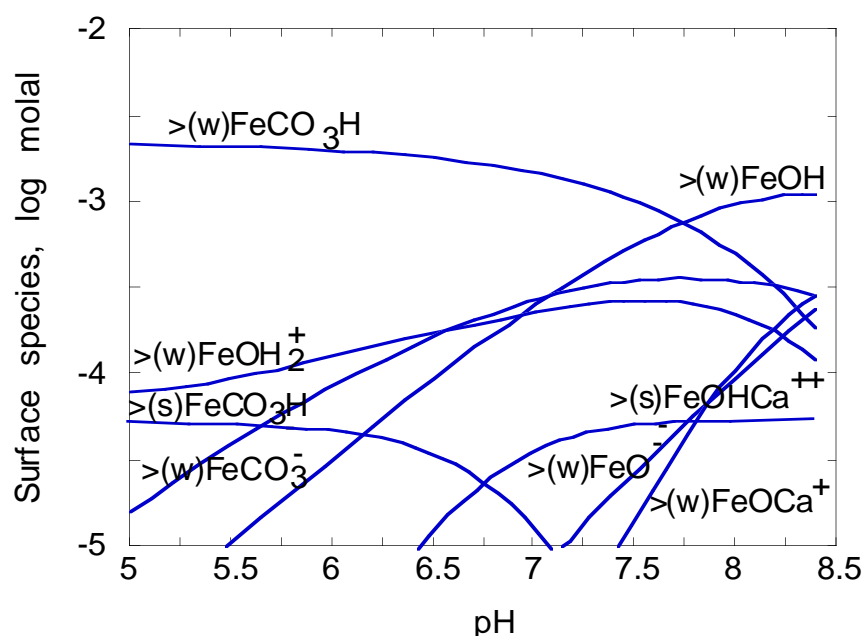
Figure 2b. Concentration of surface complexes on 1 g goethite/kg H_2O in HBH02 water at 25°C using Dzombak and Morel (1990) data with carbonate surface species from Van Geen, Robertson and Leckie (1994). Electrical balancing on HCO_3. Concentration of surface complexes expressed as moles of complex per kg of H_2O, i.e. molality.

Table 1. Predicted sorbed fractions and concentrations of Ca, Sr and SO_4 (in mg/kg) in HBH02 as a function of mass of goethite/kg H_2O. Calculated using Dzombak and Morel (1990) surface complexation data base.

Mass of goethite (g/kg H_2O)	Predicted sorbed fraction and concentration (in parentheses) of sorbed species. Concentrations expressed in mg/kg.		
	Ca	Sr	SO_4
0.1	0.0013 (0.057)	0.0014 (0.0002)	0.1 (2.2)
1	0.013 (0.57)	0.014 (0.002)	0.53 (21.7)
10	0.12 (5.66)	0.12 (0.02)	0.92 (215.7)
Concentration in coexisting fluid phase, mg/kg	42.8	0.16	19.5

Table 2. Predicted sorbed fractions and concentrations of sorbed Ca, Sr, SO_4 and HCO_3, in mg/kg, in HBH02 as a function of mass of goethite/kg H_2O. Calculated using Dzombak and Morel (1990) surface complexation data base with carbonate complexation constants from Van Geen, Robertson and Leckie (1994).

Mass of goethite (g/kg H_2O)	Predicted sorbed fraction and concentration (in parentheses) of sorbed species. Concentrations expressed in mg/kg.			
	Ca	Sr	SO_4	HCO_3
0.1	0.0015 (0.06)	0.0016 (0.0003)	0.0022 (0.04)	0.09 (11.21)
1	0.015 (0.63)	0.016 (0.003)	0.022 (0.43)	0.50 (112.1)
10	0.13 (6.31)	0.14 (0.03)	0.18 (4.31)	0.91 (1121)
Concentration in coexisting fluid phase, mg/kg	42.8	0.16	19.5	114.

2.2   SORPTION ONTO HFOs IN NATIVE (DEEP) WATERS

2.2.1 Calculations using surface complexation data base excluding carbonate surface species

The elements predicted to be sorbed onto goethite in equilibrium with KA0483A water are shown in Figure 3a as a function of pH using the carbonate surface species-free data base of Dzombak and Morel (1990). 1 gram of goethite was assumed to be in contact with 1 kg of H_2O with the solution composition of KA0483A. The identity and molality of the surface species as a function of pH are shown in Figure 3b. Table 3 summarizes the predicted sorbed fractions and the concentrations of sorbed components as a function of the sorbent:fluid ratio.

Predicted sorbed fractions for Ca, Sr and SO_4 (Table 3) are less than those predicted for HBH02 (Table 1), although the concentrations of sorbed species are larger for a given sorbent:fluid ratio. KA0483A water contains less HCO_3 than HBH02, but greater quantities of Ca and SO_4. Thus, even though the calculated sorbed fraction of Ca and SO_4 may be less than that predicted to be in equilibrium with HBH02, the absolute quantities of sorbed species may actually be greater. For example, greater quantities of Ca are sorbed at alkaline pH onto HFO in equilibrium with KA0483A, but the calculated sorbed fraction of Ca is less than that predicted for HBH02 because KA0483A waters contain more Ca. The above discussion demonstrates that predicted sorbed fractions must be interpreted with care.

2.2.2 Calculations using surface complexation data base including carbonate surface species

The impact of including carbonate surface species using data from Van Geen, Robertson and Leckie (1994) is shown in Figures 4a and 4b for comparison. Table 4 details the predicted sorbed fraction and the concentrations of sorbed components as a function of the sorbent:fluid ratio. As in the HBH02 simulations, the sorbed fraction of carbonate surface complexes dominates that of sulfate complexes. The sorbed fraction of carbonate exceeds 0.5 when the mass of goethite exceeds 1 gram per kilogram of H_2O. This means that a greater reservoir of carbonate may be associated with HFOs than with the fluid, as was predicted for HFOs in equilibrium with HBH02 water.
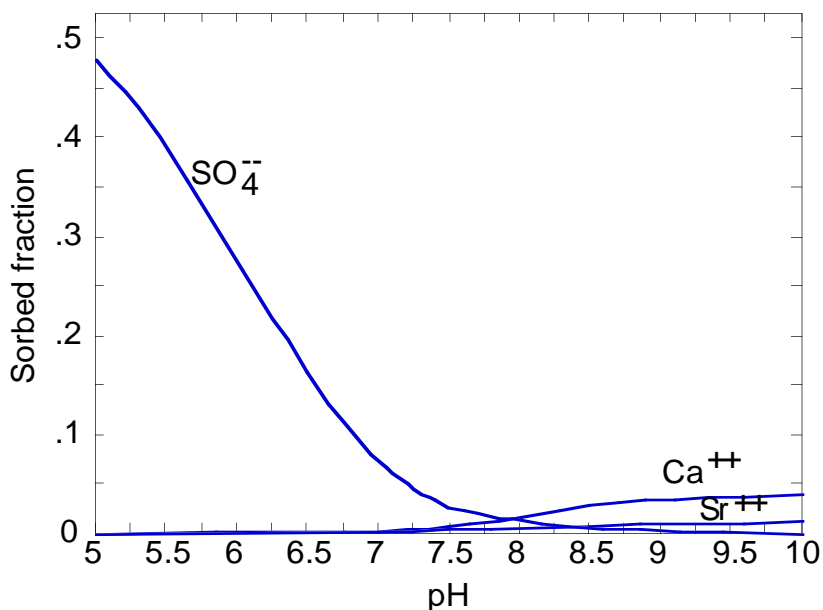
Figure 3a. Fraction of total quantity of SO₄, Ca and Sr sorbed onto 1 g goethite/kg H₂O in HBH02 25°C using Dzombak and Morel (1990) surface complexation data base. Electrical balancing on Cl.
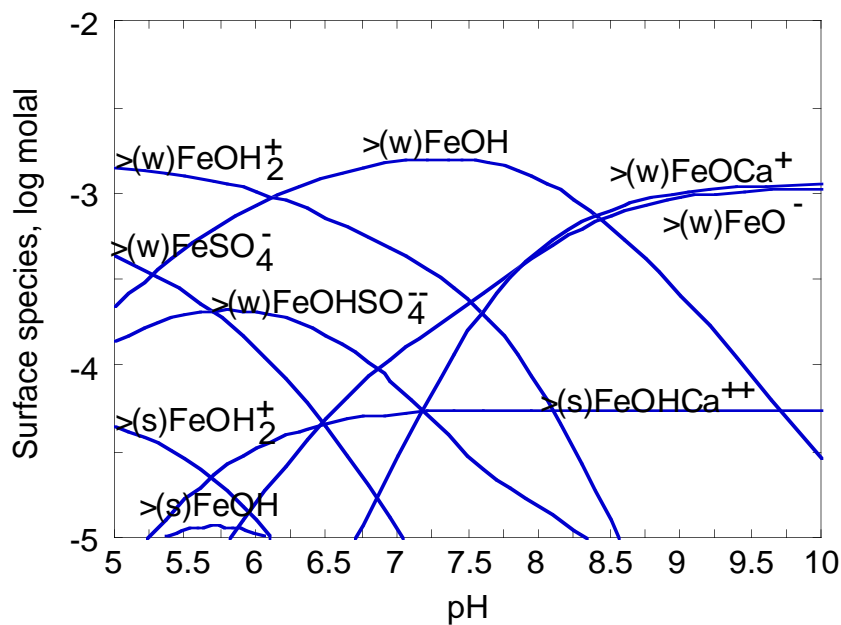

Figure 3b. Concentration of surface complexes on 1 g goethite/ KA0483A water at 25°C using Dzombak and Morel (199 complexation data base. Electrical balancing on Cl. Concentration complexes expressed as moles of complex per kg of H₂O, i.e. molal
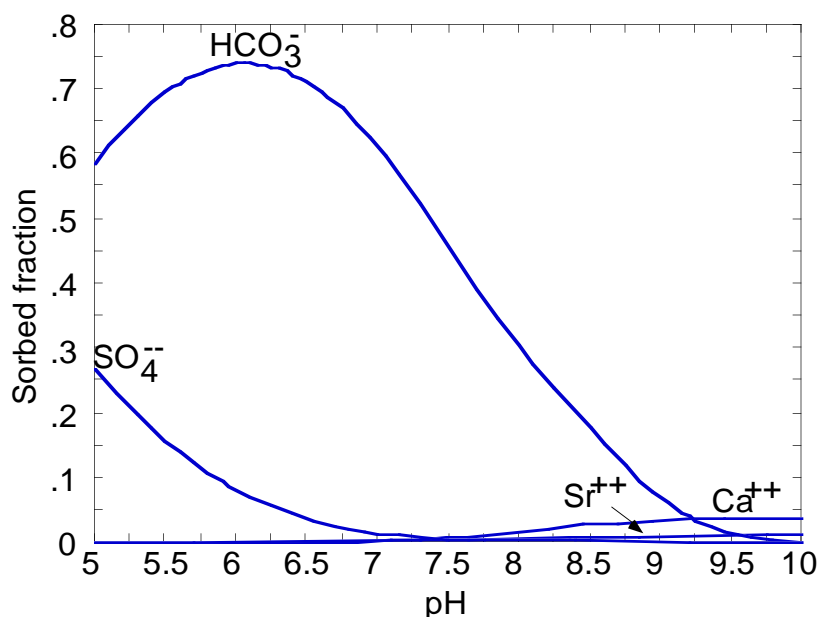
Figure 4a. Fraction of total quantity of HCO_3, SO_4, Ca and Sr sorbed onto 1 g goethite/kg H_2O in KA0483A water at 25°C using Dzombak and Morel (1990) surface complexation data with carbonate surface species from Van Geen, Robertson and Leckie (1994). Electrical balancing on Cl.
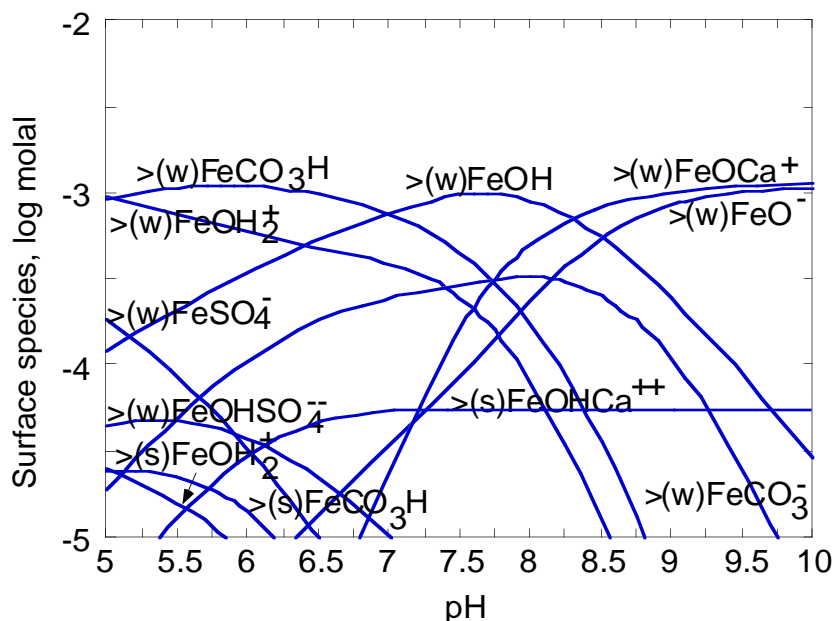

Figure 4b. Concentration of surface complexes on 1 g goethite/kg H_2O in KA0483A water at 25°C using Dzombak and Morel (1990) data with carbonate surface species from Van Geen, Robertson and Leckie (1994). Electrical balancing on Cl. Concentration of surface complexes expressed as moles of complex per kg of H_2O, i.e. molality.

Table 3. Predicted sorbed fractions and concentrations of sorbed Ca, Sr and SO4, in mg/kg, in KA0483A as a function of mass of goethite/kg H2O. Calculated using Dzombak and Morel (1990) surface complexation data base.

Mass of goethite (g/kg H2O)	Predicted sorbed fraction and concentration (in parentheses) of sorbed species. Concentrations expressed in mg/kg.		
	Ca	Sr	SO4
0.1	0.0007 (0.83)	0.0003 (0.0007	0.003 (0.18)
1	0.007 (8.33)	0.003 (0.07)	0.029 (1.79)
10	0.063 (83.15)	0.03 (0.68)	0.23 (17.82)
Concentration in coexisting fluid phase, mg/kg	1250	21.5	60

Table 4. Predicted sorbed fractions and concentrations of sorbed Ca, Sr, SO4 and HCO3, in mg/kg, as a function of mass of goethite/kg H2O in KA0483A. Calculated using Dzombak and Morel (1990) surface complexation data base with carbonate complexation constants from Van Geen, Robertson and Leckie (1994).

Mass of goethite (g/kg H2O)	Predicted sorbed fraction and concentration (in parentheses) of sorbed species. Concentrations expressed in mg/kg.			
	Ca	Sr	SO4	HCO3
0.1	0.0007 (0.87)	0.0003 (0.007)	0.0008 (0.05)	0.09 (3.96)
1	0.007 (8.7)	0.003 (0.07)	0.008 (0.5)	0.49 (39.6)
10	0.066 (87)	0.032 (0.7)	0.078 (5)	0.91 (396)
Concentration in coexisting fluid phase, mg/kg	1250	21.5	60	42

3.   DISCUSSION

In order to relate the calculations described in this paper to attributes of natural systems, we must establish the relevance of the masses of goethite used per kg H_2O. For a given fracture width, we calculated the thickness of a continuous goethite fracture coating yielding 0.1, 1 and 10 grams of goethite per kg H_2O, assuming a fully saturated system (Figure 5). The number of surface sites corresponding to 0.1, 1, and 10 grams of goethite are also shown in Figure 5.

Given the abundance and distribution of HFOs observed at Äspö, the quantities of goethite used per kg of H_2O seem reasonable. The masses of goethite used in the calculations were not, however, originally selected through an analysis of HFO occurrence at Äspö. Even though the goethite does not form continuous surface layers in nature, the calculation nonetheless demonstrates that the masses of goethite considered in this report are conservative, yet account for a great deal of surface complexation.

The number of sites available for surface complexation reactions was calculated assuming 0.205 mol of sites/mol Fe, which is equal to 0.205 mol sites/mol goethite (Dzombak and Morel, 1990). This is equivalent to 2.31×10^{-3} moles of surface sites per gram of goethite.

The results of geochemical simulations such as those described in this paper are only as reliable as the surface complexation constants and the complexation model upon which the predictions are based. For example, the carbonate complexation constants from Van Geen, Robertson and Leckie (1994) may overestimate the degree of formation of surface carbonate complexes. If so, the degree of SO_4 sorption would increase.

The reliability and robustness of surface complexation models and their data bases in simulating controlled and natural systems has not yet been explored fully. The results in this paper should therefore not be used at this time as absolute, quantitative predictions of system behavior, but rather as a guide to how systems will behave in response to a change in the physical and/or chemical state such as induced by fluid mixing or changes in pH and redox state.
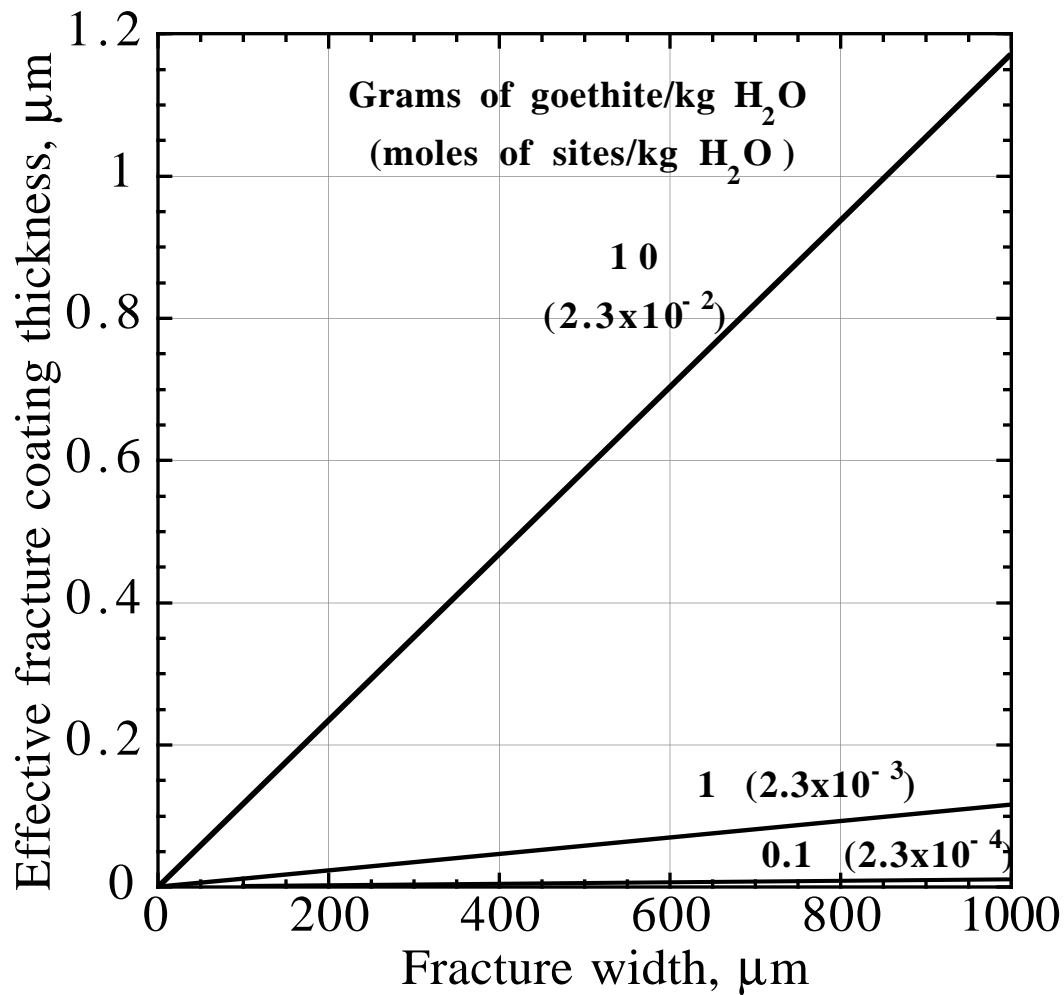
Figure 5. Effective thickness of fracture coating of goethite required to allow 0.1, 1 and 10 grams of goethite to contact 1 kg of H_2O contained within the fracture. Corresponding moles of surface sites/kg of H_2O also shown for reference.

4.   FLUID MIXING SIMULATION

4.1   METHOD

The mixing of a shallow water represented by HBH02-910912 (Banwart et al., 1992) and a deep native water represented by KA0483A-910312 (Banwart et al., 1992) was simulated with the computer code React (Bethke, 1994). The end member waters are the same as those used by Viani and Bruton (1994).

Fluid mixing in React was conducted differently than in Viani and Bruton (1994), who used EQ3/6, owing to differences in code capabilities. In React, the mixing of increasing amounts of shallow fluid (HBH02) into the deep fluid (KA0483A) was simulated by

1) specifying the composition of the deep fluid per kg of solvent (H_2O).

2) specifying the mass and composition of the shallow fluid that will be gradually mixed with the deep fluid.

3) removing or "flushing" from the system a mass of the deep fluid/shallow fluid mixture equivalent to each increment of shallow fluid that is added, to retain a total mass of H_2O of 1 kg. (In the EQ3/6 simulation of Viani and Bruton (1994), an equivalent mass of the original, unmixed deep fluid was removed.)

Ten kg of the shallow fluid were flushed into 1 kg of the deep water system. This mass was chosen so that the final ionic strength is close to that of the shallow fluid. Fluid mixing was assumed to occur in the presence of 1 gram of goethite per kilogram of H_2O.

4.2   RESULTS

The predicted concentrations of Ca, Sr and SO_4 in the aqueous phase do not vary significantly from the concentrations that are predicted using a conservative fluid mixing model. Results for HCO_3 are more difficult to interpret and cannot be addressed adequately at this time. However, it appears that for major elements such as Ca and SO_4, surface complexation onto HFOs during mixing of shallow and deep waters does not account for observed deviations from a conservative mixing model, at least for the ranges of sorbent:fluid used in the calculations.

Future studies will explore the impact of fluid mixing on the distributions of trace elements such as uranium at Äspö.

5   <u>CONCLUSIONS</u>

Hydrous ferric oxides are important sources and sinks of carbonate in both the shallow and deep, native waters at Äspö through surface complexation. Carbonate surface complexation is favored over sulfate surface complexation at neutral to acid pH. Ca and Sr sorption increase as pH increases.

Geochemical modeling of surface complexation on goethite, used as a proxy for HFOs, suggests that a greater reservoir of carbonate may be associated with HFOs than with the fluid. For example, 1 to 20 times the mass of aqueous carbonate can be sorbed onto 1 to 10 grams of goethite in approximately 1 kg of both shallow HBH02 and deep KA0483A water. Thus, HFOs may serve as important sources and sinks of carbonate. Comparatively small amounts of Ca and Sr are sorbed from the shallow HBH02 water and the deep KA0483A water.

The sorbent:fluid ratios used to evaluate the effects of sorption on fluid chemistry are consistent with observations of HFO abundance at Äspö. Geochemical simulations of mixing between HBH02 and KA0483A waters suggest that major elements such as Ca , Sr and SO_4 are not significantly affected by surface complexation onto HFOs. Thus, surface complexation does not account for observed deviations from a conservative mixing model for Ca and SO_4, at least for the ranges of sorbent:fluid ratios used in the calculations.

Future studies should explore the impact of fluid mixing on the distributions of trace elements such as uranium at Äspö. A sorption data base for uranium is available (Waite et al., 1994), but effort will be required to develop or estimate sorption data for other trace elements that have been measured in Äspö waters (e.g., Nilsson, 1995).

6   <u>ACKNOWLEDGMENTS</u>

7   REFERENCES

Banwart, S., Laaksoharju, M., Nilsson, A-C., Tullborg, E-L. and Wallin, B., 1992. The Large Scale Redox Experiment: Initial characterization of the fracture zone, <u>SKB Äspö Hard Rock Laboratory Progress Report 25-92-04</u>, Stockholm.

Banwart, S., Gustafsson, E., Laaksoharju, M., Nilsson, A-C., Tullborg, E-L. and Wallin, B., 1994. Large-scale intrusion of shallow water into a vertical fracture zone in crystalline bedrock: Initial hydrochemical perturbation during tunnel construction at the Äspö Hard Rock Laboratory, southeastern Sweden. Water Resources Res., v. 30, p. 1747-1763.

Laaksoharju, M., 1994. Mixing calculations: A first step in the modeling of a natural groundwater system. In Banwart, S., ed., <u>Proc. Äspö International Geochemistry Workshop</u>, June 2-3,1994, Äspö Hard Rock Laboratory, p. B-57-B-66.

Landström, O. and Tullborg, E-L., 1995. Interactions of U, Th, REE, Ra, Cs and Sr with clay minerals, Fe-oxyhydroxide and calcite, draft.

Nilsson, A-C., 1995. Compilation of groundwater chemistry data from Äspö: 1990-1994, <u>SKB Äspö Hard Rock Laboratory Progress Report 25-95-02</u>, Stockholm.

Tullborg, E-L., 1995, Mineralogical and chemical data on rocks and fracture minerals from Äspö, <u>Äspö Hard Rock Laboratory Technical Note 25-95-07g</u>, Stockholm.

Van Geen, A., Robertson, A.P. and Leckie, J.O., 1994. Complexation of carbonate species at the goethite surface: Implications for adsorption of metal ions in natural waters. Geochim. et Cosmochim. Acta, v. 58, p. 2073-2086.

Viani, B.E. and Bruton, C.J., 1994. Effect of cation exchange on major cation chemistry in the Large Scale Redox Experiment at Äspö. In Banwart, S., ed., <u>Proc. Äspö International Geochemistry Workshop</u>, June 2-3, 1994, Äspö Hard Rock Laboratory, p. B-78-B-96.

Waite, T.D., Davis, J.A., Payne, T.E., Waychunas, G.A. and Xu, N., 1994. Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model, Geochim. et Cosmochim. Acta, v. 58, p. 5465-5478.

Appendix A. **Surface complexation constants (K)**

Surface complexation reaction	log K		
	Dzombak and Morel	Waite et al. I=0.1	Van Geen et al.- intrinsic
$>FeOH + H^+ = >FeOH_2^+$	7.29*	6.51*	7.91
$>FeOH = FeO^- + H^+$	-8.93*	-9.13*	-10.02
$>FeOH + H^+ + HCO_3^- = FeCO_3H^o + H_2O$	--	9.266*	10.45
$>FeOH + HCO_3^- = FeCO_3^- + H_2O$	--	1.276*	2.38
Model	Gen. Diffuse double layer; 2-site	Diffuse double layer; 2-site	Diffuse double layer; 1-site
Site density	2.3 sites/nm^2	9.88 sites/nm^2 (calc.)**	2.3 sites/nm^2
Sites	0.205 mol/mol Fe; 0.2w,0.005s	0.875 mol/mol Fe;0.0018w	0.015 mol/mol Fe (calc.)**
Surface area	600 m^2/g	600 m^2/g	45 m^2/g

* reaction constants for weak and strong surface sites assumed to be equal
** calculated from data in paper